Referee 1

We thank the reviewer for their constructive comments which have helped to improve the manuscript. Below we have outlined point by point the responses to each comment:

The authors present a detailed and novel study of nitrogen dynamics within six major Arctic rivers through collection of water samples analyzed for dissolved nitrogen species and nitrogen isotope values. These six rivers span a gradient of permafrost coverage throughout the watershed with the Kolyma having the most continuous permafrost coverage to the Ob which has the least permafrost coverage. Major findings include large inputs of DON and nitrate with isotopically heavy ^{15}N signature due to the Yedoma permafrost thaw zones along the Kolyma. Evidence for permafrost derived DON being recycled to nitrate is presented within this watershed. The authors also present a great data set on seasonal nitrogen dynamics within the six rivers even though the impacts of permafrost degradation could not be shown in this study. Instead, fresh DON from surface runoff and most likely lateral flow through the organic rich top-soils of the watershed supplies the majority of nitrogen within these rivers. The Ob river is presented as one possible future (due to less permafrost coverage) of nitrogen dynamics for the other 5 rivers. Permafrost thaw could be identified with nitrogen isotopes only within small spatial scales due to dilution and vast catchment differences (and their processes) of the main stem rivers. The authors provide detailed discussion of how different types of permafrost thaw impact and watershed characteristics can impact nitrogen and isotopic dynamics.

In general, I would pay close attention to the use of flux and loads throughout the document, particularly with uncited language. Most of the data presented here is concentration (with one figure of flow-normalized concentration).

Figure 1. *Potentially add a table of watershed characteristics (including but beyond continuous permafrost coverage) to Figure 1. Perhaps include amount of peatland area, lake coverage, glacial coverage, etc. that is referred to throughout the article. This could also be a supplementary table*

A table showing some of the watershed information has been added

Lines 61-64
Is Zhang the original citation here? Or is it R.O. van Everdigen, Multi-language glossary of permafrost and related ground-ice terms Definitions (1998), p. 78.
I would probably use the van Everdigen reference in place of the Brabets reference. While that definition is included within the Brabets, I don't think it can be attributed to him.

Thank you for the correction, the van Everdigen paper has now been cited here

68-77
Seems like there are some citations missing here.

Added two references, Streletskiy et al., 2015 and Beermann et al., 2017

78-90

It would be nice to mention some of the limitations and uncertainties associated with these studies.

A mention of some uncertainties has been added

Lines 195-196
The authors could remove the last sentence of this paragraph as they reference the fluid mud stream in line 193.

Changed the wording to make it clearer that samples for this study were collected from a similar fluid mud stream

Line 216- *add "the" between capturing and variability*

Done

Lines 218-220 *It would be good to cite some of the studies regarding the limitations/variability of these discharge records for these rivers*

A few citations have been added addressing the reliability and accuracy of these discharge records and predictions

Figure 2- *"Continuous" is misspelled on each of the X axes within this figure.*

This has been corrected in the figure, thanks for pointing this out

Figure 3*-It might be beneficial to add a secondary Y axis or a second panel to better capture the small scale differences referred to in the text (Lines 290-321)*

An insert plot showing the small scale changes has been added to this figure

Figure 5-*Great figure!*

Thanks!

Figure TK *I think it would be beneficial to have a conceptual figure the visualizes the how different permafrost conditions and other catchment factors influence the nitrogen cycle, isotope fractionation either at this point or earlier in the article. There is a lot of text within the article that does a great job of describing all of these processes, however, you might be able to significantly reduce the amount of text by referencing a new Figure that visually represents these processes and impacts.*

Thank you for the suggestion. However, I feel that this figure might be a little complicated/cluttered to show all of the processes at play. There are many interlinking factors that can affect the nitrogen cycle and associated isotopic fractionations and trying to distil them into a figure might lead to oversimplified view of the underlying processes. The purpose of this paper was to outline some specific processes occurring in permafrost degradation zone and how it changes downstream, not to show how all possible factors affect the nitrogen cycle. Although some suggestions have been made in the text as to the full controlling factors and I agree that it would be beneficial to have this conceptual figure, the data produced from this study wouldn't really allow a full picture to be shown.

Figure 6- *Yukon X axes for both nitrate and discharge differ slightly from all other rivers (or at least the labeling does). I would also include the years of 2003-2018 within the title of this figure. I wonder if spot calculating loads/flux here for DON and NO_3 might provide some interesting insights, especially since the authors*

The x axes and the title have been changed in the figure.
Calculations of fluxes/loads were done originally in this study but after discussion with co-authors it was decided that these should not be included. The reasoning for this was that to compare results with other ArcticGRO published data, fluxes/loads needed to be calculated using the USGS LOADEST software. This required a minimum of n=12 data points which was more than the six data points per year in the sample set of this study. Including the fluxes also didn't change the overall interpretation of the results and the conclusions drawn.

Line 494, *I would move the citation of Figure 1 to Line 493 after 'rivers'. As it reads, to me, it suggests that Figure 1 is a nitrogen cycling figure.*

Done

Line 550- *is this percolation? Or lateral subsurface flow?*

Percolation as the groundwater can move to greater depths vertically through the horizons. However, also added that the lateral subsurface flow will be deeper with a lack of permafrost.

Line 616- *is this "of riverine nitrogen geochemistry" or on?*

Changed to "on riverine nitrogen geochemistry"

Referee 2

We thank the reviewer for their constructive comments which have helped to improve the manuscript. Below we have outlined point by point the responses to each comment:

The manuscript by Francis et al. presents an interesting study on the extent of permafrost degradation effects on nutrient speciation, cycling and processes in Artic rivers using isotopes. It is a comprehensive study and the sampling design is well-thought of, taking into account both spatial (catchment versus permafrost degradation zone) and temporal scales. On a catchment scale, the authors found that the extent of permafrost coverage was controlling the variability of nitrate but not DON – an important finding which also suggests the potential impact of climate change on nutrient dynamics through permafrost degradation. The permafrost thaw exhibited distinctive isotopic signatures of nitrate and DON which significantly inferred the applicability of isotopes in identifying the transport pathways of nutrient either via surface runoff or subsurface flows. The dynamics of nitrate, DON and associated isotope values downstream of that zone suggested a combination of physical (dilution) and biogeochemical processes (mineralisation, denitrification, nitrification) although disentangling the contributions of these processes require further studies. Overall, the manuscript is well-written and their ideas are well-articulated but the manuscript could be more concise (particularly the introduction) and clearer in some places. See below for more specific comments:

The introduction has been made a little more concise by rewording and also removing some sections not completely relevant to this study.

Line 68: *Be more consistent with the term used throughout the manuscript especially when the terms indicate the same meaning, e.g. thaw versus degradation, intact versus continuous?*

The terminology has been changed to ‘degradation’ and ‘continuous’ throughout. Including the figures PT to PD and PI to PC

Line 100-106: *The sentences here seem contradicting. At first, the authors indicated that with limited permafrost thaw, nitrogen export is predominantly DON then later on, when permafrost begins to thaw (which to me indicates more permafrost thaw), DON concentrations in streams increased rapidly. Is the timing of thawing that affects the variability of DON or is it the extent of permafrost thaw that is the controlling factor? Be clearer here?*

I agree that these sentences are a little confusing. I have reworded it to state that with limited permafrost degradation DON is preferentially released over nitrate at relatively low concentrations but as more permafrost degradation occurs, both species will be released but DON to a much greater extent with the ratio of DON: Nitrate increasing. The extent of permafrost degradation is the controlling factor on DON variability as greater depths of soil are exposed with increasing degradation.

Line 107: *While it is discussed in the introduction that peat layer is also an important factor affecting the preferential flow/transport of nutrients but this information was not presented for the study sites. Suggest including this piece of information in site description given its importance in controlling the transport mechanism and thus the variability of nutrients within the catchment.*

Peat depths and horizon types are important for certain catchments where active layer deepening is the primary permafrost degradation mechanism. Kolyma has mainly an erosional style degradation mechanism so has both organic layer and mineral influence in dissolved nitrogen additions. Information on this has been added to the site description of the Kolyma local scale site. Peat depth estimates have also been added to a table of catchment descriptions in figure 1.

The manuscript does mention that results from the local scale Kolyma site would likely be different where a different degradation mechanism is occurring. I have added a bit stating that here the depth of peat would play a more important role in interactions with different soil horizons.

Line 174: *Was the sample collected from the same site for Kolyma at two different scales (i.e. catchment vs. PT zone)?*

Samples for the catchment scale were collected at the specific sites outlined in the ArcticGRO site data and the local scale permafrost degradation sample was collected further upstream from an area draining degrading permafrost. The instream samples labelled R1 was the same site as the catchment scale ArcticGRO site. I have made this clearer in the text.

Line 177: *Is there a specific reason why samples were filtered through 0.7um filters and not smaller pore-sized filters (i.e. 0.45um and 0.2um) as the common procedure for collecting dissolved nutrient and isotope samples?*

0.7um is the nominal pore size of the GF/F filter which is commonly used for all DOM work. These filters can be combusted to eliminate the risk of organic contamination and there is no GF/F pore size standard between 0.2 and 0.7um. Many studies use cut-offs across those ranges with comparable data e.g. see Denis et al. 2017 (https://doi.org/10.1016/j.orggeochem.2017.05.002) or Voss et al. 2011 (https://doi.org/10.1016/B978-0-12-374711-2.00508-8)

Line 243: *Given the persulfate digestion could potentially introduce fractionation if recovery of the conversion is not close to 100% (which is very likely). Was there any standard (internal?) used in this method to ensure that fractionation is minimal and is representative of the actual d15N of DON.*

Yes, two organic standards were used to monitor this, USGS40 and an internal Glycine-standard. Additionally blanks of potassium persulphate solution were run to check for any nitrate contamination/isotopic signatures remaining after triple recrystallization. The percentage contribution of the blank to the final d15N value was checked and corrected accordingly. The final d15N values for the two internal standards, (that had undergone the same digestion and correction process) were checked for any fractionation effects with the d15N values (USGS40 = -4.5‰, Glycine = 1.1‰, (Dumont, 2019))

Line 254: *Were ammonium concentrations measured in this study or it was assumed that ammonium was negligible? Referring to Holmes et al. 2012, ammonium concentrations were much higher than nitrate in all the studied Russian rivers draining into the Arctic Ocean almost throughout their study period. Given the high DON concentrations and low nitrate particularly in the permafrost thaw zone, there is a possibility that ammonium could be present and could significantly affect the isotopic values of TDN. Without the concentration data, I don't think the assumption that d15N-DON is the difference in concentration weighted isotopic values between TDN and NO3 can be justified, particularly in the permafrost thaw zone.*

Holmes et al. 2012 states "On all rivers except the Ob' and Yukon, there were not enough NH4-N measurements above the detection limit to meet the minimum LOADEST requirement for uncensored data points". If ammonium concentrations were above detection they were nearly always much lower than nitrate concentrations. This can be observed in the Arctic GRO online database.

Ammonium concentrations were not measured on the local scale Kolyma river. But due to the fact that ammonium is very labile, short lived and quickly converted into nitrite/nitrate in peatlands, the assumption that d15N-DON is the difference in concentration weighted isotopic values between TDN and NO3 can be justified.

Line 359: *Why would d15N be lower in this case? You meant the preserved organic matter had low d15N to start with? If yes, then be more specific here*

Yes, this is what was meant when describing the lower d15N. I have clarified the wording in the text:

“Additionally, the fact that DON is not isotopically heavier than nitrate is also expected as the primary source of DON is from decaying organic matter preserved in the permafrost and this process releases organic matter with a low δ15N to start with that forms DON also with a lower δ15N (Sipler and Bronk, 2015).”

Line 369: *d18O ‘resets’ not just to ambient water but dissolved oxygen as well unless DO did not vary throughout the study period*

I have added this point in. “The δ18O-NO3- signal ‘resets’ to the value of ambient water and dissolved oxygen when it is recycled (Buchwald and Casciotti, 2010)”. DO didn’t vary much downstream in the main stem of the Kolyma where recycling continued.

Line 504, 563, 608, Fig. 8: *A few other places are confusing – whether the samples were analysed or just solely based on assumption/literature values e.g. soil, groundwater and water isotopes. If they were being measured, include the description in the method sections. If the values were taken from the literature, then these should be referenced appropriately.*

Line 504 has been modified to include its reference source but it is also partly an assumption based on this study and literature

Line 608 has been updated to include its reference source

Line 563 and Figure 8 is an interpretation for nitrate sources through the year based on the results of this study as outlined in the text above it. This has been made clearer in the figure caption.

Figure 2b:

(1) Y-axis for (i) – DON instead of nitrate?

Yes, that should indeed be DON instead of nitrate. This has been changed, thanks for noticing.

(2) Standard deviation for the concentration averages?

This has been added

(3) I am wondering if there is any relationship between the isotopes of nitrate, DON and % catchment with continuous permafrost. I believe the authors might have considered this and have found no relationships?

There were no available datasets for nitrogen isotopes of ArcticGRO data covering the same time period as figure 2 (2003 to 2018). The data generated from this study could not be averaged for nitrogen isotopes for all rivers due to an incomplete seasonal dataset for the Lena and Yenisey (as described in figure 7). Therefore plotting isotopes of nitrate, DON and % catchment vs continuous permafrost was not possible.

Figure 3: *Considering breaking the y axis for PT data so concentrations of other samples are visible on the plot. Another suggestion is to present the ratio of DON to nitrate concentrations. This will make it easier for the readers to follow*

An insert plot showing the small scale changes has been added to this figure. However, I don't think that using the ratio of DON to nitrate on the plot would be that beneficial for interpretation due to the very small concentrations of nitrate relative to DON.

Figure 7: *(a)-Kolyma, what is the dotted line for?*

That is a mistake and somehow made it into this version of the figure. It has been removed.

Suggest combining Figure 3 and 4 into a plot with three panels (a) d18O versus d15N (b) d15N-TDN versus TDN conc (c) d15N-DON versus DON conc. This will make it easier for the readers to follow and compare the concentrations and isotopes of different analytes.

Thanks for the suggestion. However, I don't think the inclusion of these plots particularly adds to the conclusions drawn from the original figures. The main points that are being expressed are:

- The permafrost degradation zone has a hugely greater concentration of TDN, DON and nitrate than the permafrost influenced sites and in the river/estuary.
- That DON concentrations are much greater than nitrate in all sites.
- The isotopic data shows the difference between the sites and N species, again with the permafrost degradation site being different and nitrate having a heavier isotopic signal than DON.
- A unique signal representing inputs from degrading Yedoma permafrost can be detected
- The signals observed in the permafrost degradation site were rapidly lost in the main stem of the river and into the estuary
- The concentration and isotopic signal in the river and estuarine site generally don't show much downstream change.
- The exact concentration and isotopic values of each species at each site

I think these plots make it straightforward to see these points and I believe that changing the figures to the three panels suggested wouldn't make it that much clearer to see.

***Citation**: https://doi.org/10.5194/egusphere-2022-671-RC2*

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